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Chemical Interaction between Nickel and Manganese at Various Temperatures in Ternary Solid Solutions Based on Copper

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A whole series of studies has been devoted to the question of chemical interaction between dissolved components in ternary metallic solid solutions ([1–6]), in which anomalous deviations have been established on the curves of concentration dependence of various physicochemical properties in the composition region corresponding to the intersection of the sections investigated with the corresponding quasibinary ones. It should be noted, however, that in all the systems investigated, in equilibrium with the solid solution there was a stable, congruently melting chemical compound (for example, Mg_2Si in the Al–Mg–Si system or Cr_2Zr in the Cu–Cr–Zr system). In this case it was possible only to judge the presence or absence of chemical interaction between dissolved components in the corresponding ternary solid solutions on the basis of analysis of the character of the chemical composition–property diagrams, and there was no possibility of controlling the interaction process, since the dissolved compound proved to be stable up to melting and in the liquid state.

In order to be able to follow the process of chemical interaction between dissolved components in a ternary solid solution, it is necessary that the melting temperature of this solution be higher than the temperature of thermal stability of the compound being dissolved.

It is precisely such a case that we have in the copper–nickel–manganese system chosen for the present investigation. This system is composed of three binary systems: copper–nickel, copper–manganese, and nickel–manganese, in which phase equilibrium at high temperatures is described by state diagrams with unlimited mutual solubility of the components ([7]). However, at lower temperatures in the nickel–manganese system in the solid state there occurs the formation of the compound NiMn (the H. S. Kurnakov phase), which is stable approximately up to 900°C. The character of the phase equilibrium in the copper–nickel–manganese system was studied in work ([8]), according to which the Cu–NiMn section is quasibinary, and the ordered phase θ' (NiMn), with a face-centered tetragonal crystal lattice, discovered in the binary nickel–manganese system at low temperatures, is also present in the structure of ternary alloys containing

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Fig. 2. Dependence of microhardness on alloy composition along the section at 90 at.% copper. 1-3–annealing respectively at 900, 700, and 500°C

Figure 2: Fig. 2. Dependence of microhardness on alloy composition along the section at 90 at.% copper. 1-3–annealing respectively at 900, 700, and 500°C

up to $\sim$ 86 wt. % copper.

For the purpose of investigating the character of the chemical interaction between nickel and manganese in ternary alloys at various temperatures, alloys were prepared whose compositions lay in the region of the ternary solid solution based on copper along sections intersecting the quasibinary Cu–NiMn section at 95 and 90 at. % copper*. Electrolytic copper, nickel, and manganese, remelted in vacuum $\sim 10^{-4}$ mm Hg for refining, were used as starting materials. The alloys were prepared in evacuated and sealed quartz ampoules.

* M. V. Chuprakova took part in the experimental part of the work.

After preparation, the alloys were deformed by 30-50% and homogenized at 900° for two hours. After this, chemical analysis of all alloys was carried out. Fig. 1 shows the composition of the alloys and the position of the investigated sections on the concentration triangle copper–nickel–manganese.

For elucidating the nature of the interaction between the dissolved components, the method of physicochemical analysis was employed, developed in the works of N. S. Kurnakov and his students ([9], [10]), and associated with the construction of chemical diagrams of composition–property. The microhardness of the alloys was investigated along sections whose positions are shown in Fig. 1.

Fig. 1. Composition of the alloys and position of the investigated sections on the concentration triangle copper–nickel–manganese

Earlier, using the example of copper–chromium–zirconium and copper–nickel–beryllium alloys, we showed ([6]) that, in the presence of preferential interaction between the dissolved components, significant deviations from the rule of additivity of the increment in macrohardness ([11]) are observed, reaching a maximum value when the investigated sections intersect quasibinary ones. It turned out that the dependence of microhardness in the presence of chemical interaction between alloying components is characterized not by a plane of general position, as follows from the rule of additivity, but by a surface with a clearly expressed singular fold corresponding to quasibinary sections.

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Fig. 3. Dependence of microhardness on alloy composition along the section at 95 at.% copper. 1-3—annealing respectively at 900, 700, and 500°C

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section at 90 atomic % copper. *1-3*—annealing respectively at 900, 700, and 500°C

Fig. 3. Dependence of microhardness on the composition of alloys along the section at 95 atomic % copper. *1-3*—annealing respectively at 900, 700, and 500°C

For microhardness measurements, three microsections of alloy of each composition were prepared. The finished sections were sealed in quartz ampoules evacuated to 10^{-4} mm Hg and annealed at temperatures of 900° (first batch of specimens), 700° (second batch), and 500° (third batch), respectively, for 2, 15, and 30 hours. Alloys annealed at 900° were quenched in water, while those annealed at 700 and 500° were cooled in air.

After the indicated heat treatment, the sections were etched in a 3% solution of ferric chloride in 10% hydrochloric acid according to the method described in the work—

work ([12]). Then microhardness measurements were made under a load of 50 kg. Mean values from 10-15 measurements were used. The results of the measurements are presented in the form of chemical composition-property diagrams in Figs. 2 and 3. As is evident from these figures, after annealing at 900° the dependence of microhardness on composition along the sections indicated in Fig. 1 is characterized by curves that are very close to the additive straight line (shown in Figs. 2 and 3 by a dashed line). This may indicate a random distribution of nickel and manganese atoms in the lattice of the copper-based solid solution.

The dependence obtained on alloys annealed at 700° is characterized by a serpentine-like curve with a smooth minimum in the middle and two smooth maxima at the sides. The dependence of microhardness on composition obtained on alloys annealed at 500° differs by the presence of a clearly expressed singular minimum corresponding to the intersection of the investigated sections with the quasibinary Cu—NiMn.

At the same time, the lateral maxima that are observed on the curves obtained after annealing at 700° are, in this case, expressed more sharply. The presence of a clearly expressed minimum of microhardness indicates the manifestation of preferential chemical interaction between the dissolved components ([5,6]).

Thus, from examination and comparison of the graphs given in Figs. 2 and 3, the following follows.

At 900° there is no preferential interaction between nickel and manganese; in any

case, it does not affect the character of the chemical composition–microhardness diagrams. At 500° it is strongly expressed, as is evidenced by the singular minimum of microhardness at the point of intersection of the investigated sections with the quasibinary Cu–NiMn. At 700° some intermediate state occurs.*

It is natural to assume that the observed change in the character of the chemical composition–microhardness diagrams with increasing annealing temperature is caused by dissociation of the compound NiMn, which forms in the copper-based solid solution. At 900° this compound is completely dissociated; at 500° it is probably stable, and at 700° it is partially dissociated.

It should be noted that the composition–microhardness curves obtained in the present work are, in shape, completely analogous to the curves of the concentration dependence of mechanical properties on composition in the Al–Mg–Si system, obtained by G. G. Urazov and T. I. Shushpanova ([1]), and also by N. N. Sirota and co-workers ([5]).

The presence of lateral maxima on these curves is still difficult to explain. In any case, their appearance is in no way connected with the aging process (see ([5])), since in the present case we are dealing with solid solutions lying, in composition, in that part of the concentration triangle where they are stable over the entire temperature range.

On the basis of the experimental data obtained in the present work, it may be concluded that in ternary solid solutions, as in liquid solutions (for example, aqueous ones), chemical reactions between dissolved components are possible; until now, these have not been investigated by anyone. The direction of these reactions depends on temperature and is apparently determined by the thermal stability of the corresponding chemical compound.

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* Additional annealing at 500, 700, and 900°, carried out for 40 h in order to determine the stability of the state of the alloys after the annealing indicated above, introduced no substantial changes.

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Note: Figure translations are in progress. See original paper for figures.